Jacobs Challenging today. Reinventing tomorrow.

Considerations for the Upland Remediation Strategy at the Former Citizens Gas Works MGP Site

RTA2 Gowanus Canal, Brooklyn, New York

October 18, 2021

Part 2 -NAPL immobilization perspective

NY State RAOs (for general reference)

RAOs and Goals

- Groundwater
  - Prevent, to the extent practicable, contact with, or ingestion of contaminated GW associated with the site.
  - Prevent, to the extent practicable, the migration of contaminated GW from the site.
  - Remove, to the extent practicable, the source of GW contamination.
- Soil
  - Prevent, to the extent practicable, injection/direct contact with contaminated soil.
  - Recover, to the extent practicable, DNAPL tar at the site.
- Indoor air
  - Prevent, to the extent practicable, inhalation of contaminants volatilizing from soil or GW into closed structures.

The ISGS Technology can help achieve the yellow highlighted objectives

What is the ISGS technology?

How to potentially implement at Citizen' Place?

Over-Arching Issues

- General Considerations
  - Extensive obstructions (old foundations, crib walls, utilities) limit technology selection
  - Jet grouting (ISS) may mobilize NAPL and its monolithic solids may exacerbate GW mounding
  - Permeation grouting or bentonite slurry injection have same issues.
  - Other alternatives to NAPL recovery wells and deep GW pump and treat?
- NAPL immobilization considerations
  - What approach could be used to prevent tar migration/accumulation behind bulkheads and tar off-site lateral migration?
  - How can we reduce impacts (mass transfer) of NAPL to groundwater
- NAPL leaching to groundwater considerations
  - What approach could be used to prevent shallow and deep impacted GW from migration offsite (especially in Huntington St direction?
- How and where to implement ISGS?
  - Conceptual Approach – This and other technologies require vetting

What is “In Situ Geochemical Stabilization” or ISGS?

Birnessite crust formed on roofing tar materials. Shimmer shows highly reflective precipitates

- Proprietary mix of oxidant and mineral salts
- Designed for MGP NAPL source zones
- Reacts with NAPL in hours/days forming crust and reducing NAPL mobility and dissolution, engulfing complex NAPL architecture
- Can release ISGS solution above, at or below GW and/or targeted zone
- Precipitates clog pores primarily around NAPL only, non-NAPL areas remain open / porous
- Uses a Geoprobe platform, no need for soil mixing, easy to work around obstructions, low injection pressures possible
- Excess reagent will be neutralized by peat/organic rich layers

How Provect-GS works

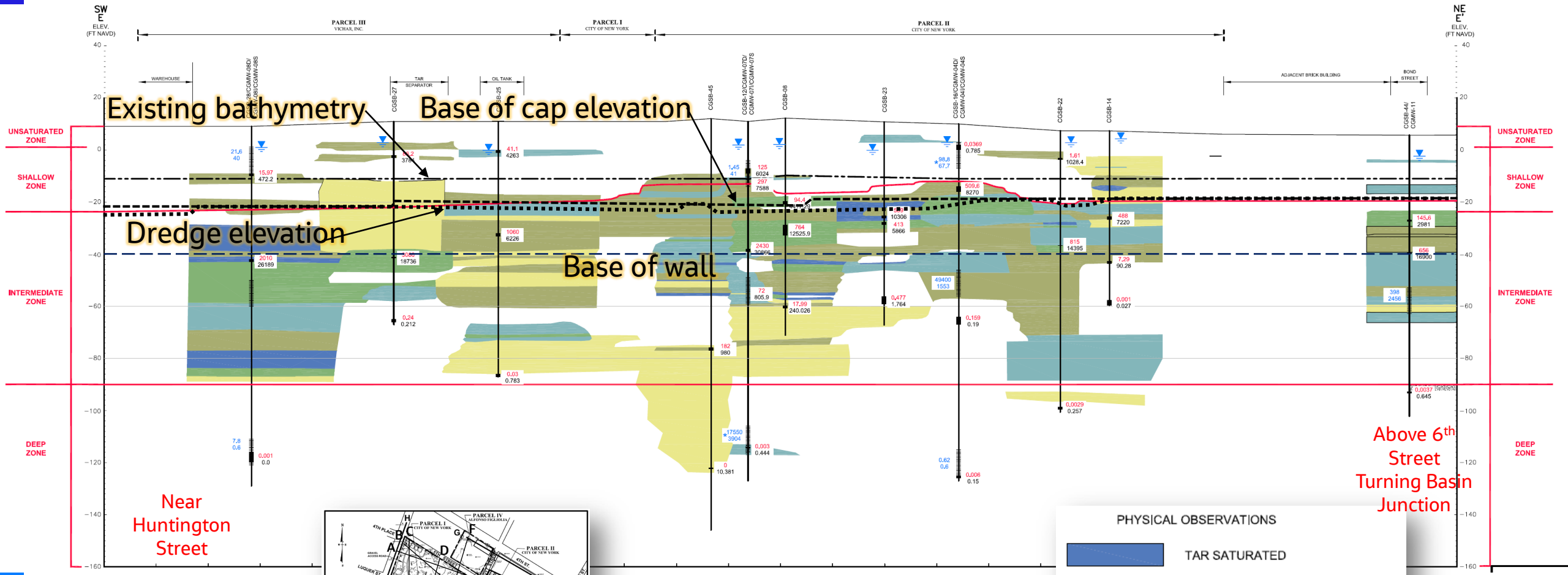
- Dry blend of mineral salts that needs to be mixed onsite to prevent settling out of solids
- Dense, water-soluble solution (SG=1.06) carries oxidant and other reagents (Fe, Si, OC) to NAPL sites
- Provect-GS has good dispersion attributes, can flow around complex NAPL structures and react with them.
- Key oxidant is a (Na/K)MnO_4, which readily dissociates in water
- Primary chemical reaction is the oxidation of organic compounds (R) which results in MnO_2 precipitation

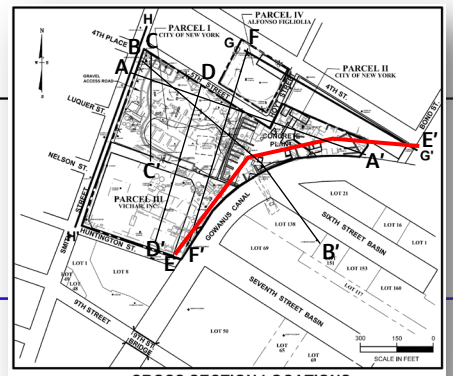
  $R + MnO_4^- \rightarrow MnO_2 + CO_2$ (or R-ox)

  where R-ox is organic intermediate if complete organics mineralization (to CO_2) does not occur

- Reactions occur at NAPL-water interface where precipitates (Mn, Fe, Si) accumulate.
  - Reduces IFT (effectively); reduces mass transfer; clogs pore space, dropping K; complex structure entrains NAPL
  - ISGS reagent diffusion into NAPL interior promotes chemical weathering/hardening and viscosity reduction since lighter fractions most prone to reaction

Citizens NAPL Observations along wall



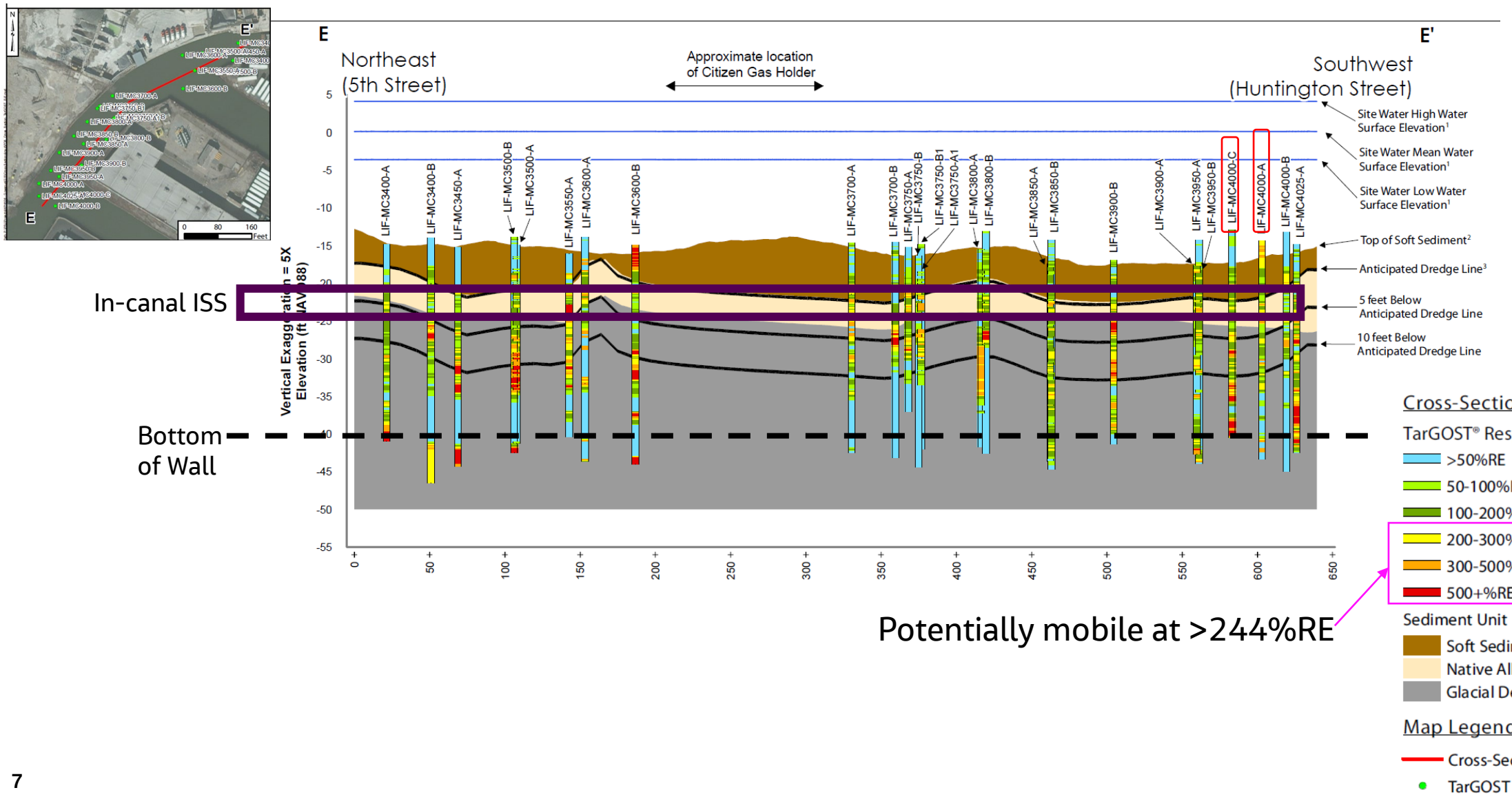


CROSS SECTION LOCATIONS

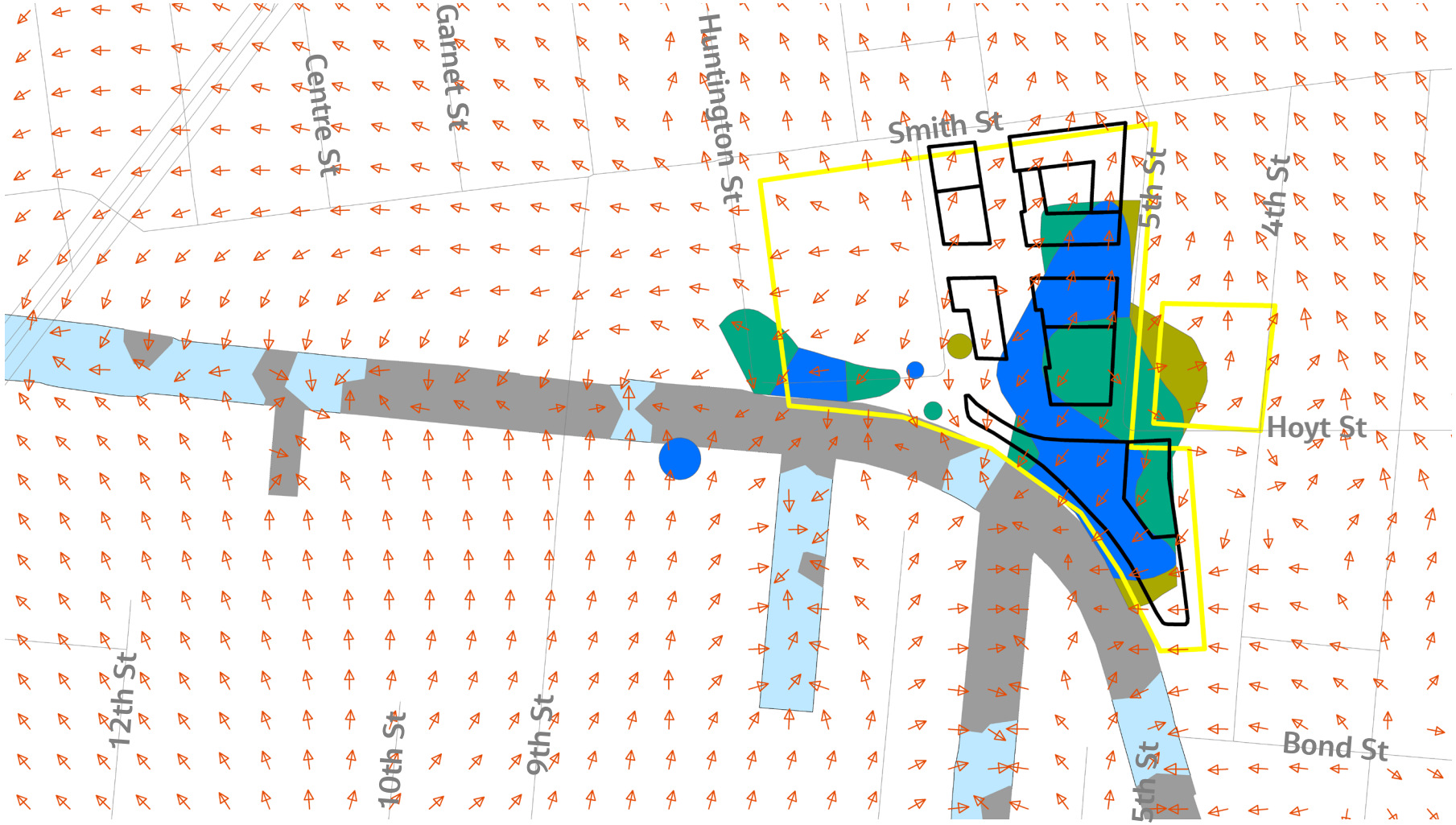
PHYSICAL OBSERVATIONS

- TAR SATURATED
- TAR STAINING, SHEEN AND TAR/NAPHTHA ODORS
- LENSES WITH TAR SATURATION AND TAR/NAPHTHA ODORS
- BLEBS, GLOBS, LENSES, COATINGS, SHEENS AND TAR/ NAPTHA ODORS
- TAR/ NAPHTHALENE-LIKE ODORS

In-canal TarGOST Impacts



Post-Remedy Groundwater Flow Directions
In-canal ISS /Alluvial Sediments Layer (L5)



LEGEND

- Post Remedy Flow Direction
- Redevelopment Area
- ISS Area of Canal
- Non-ISS Area of Canal
- Citizens Parcel Boundary

NAPL Observations

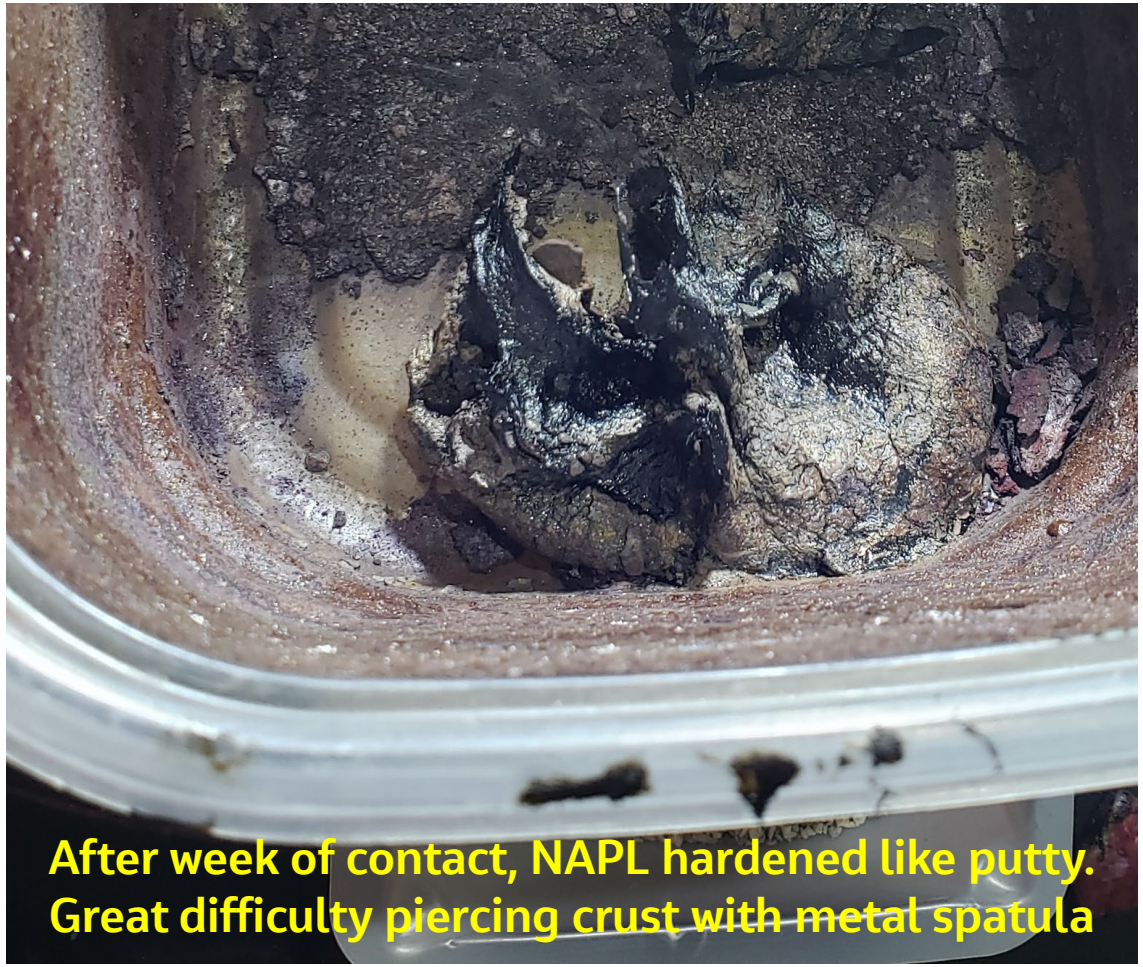
- Tar Saturated
- Lenses with Tar Saturation & Tar/Naphtha Odors
- Blebs, Globs, Lenses, Coatings, Sheens, & Tar/Naphtha Odors

N

Approximate

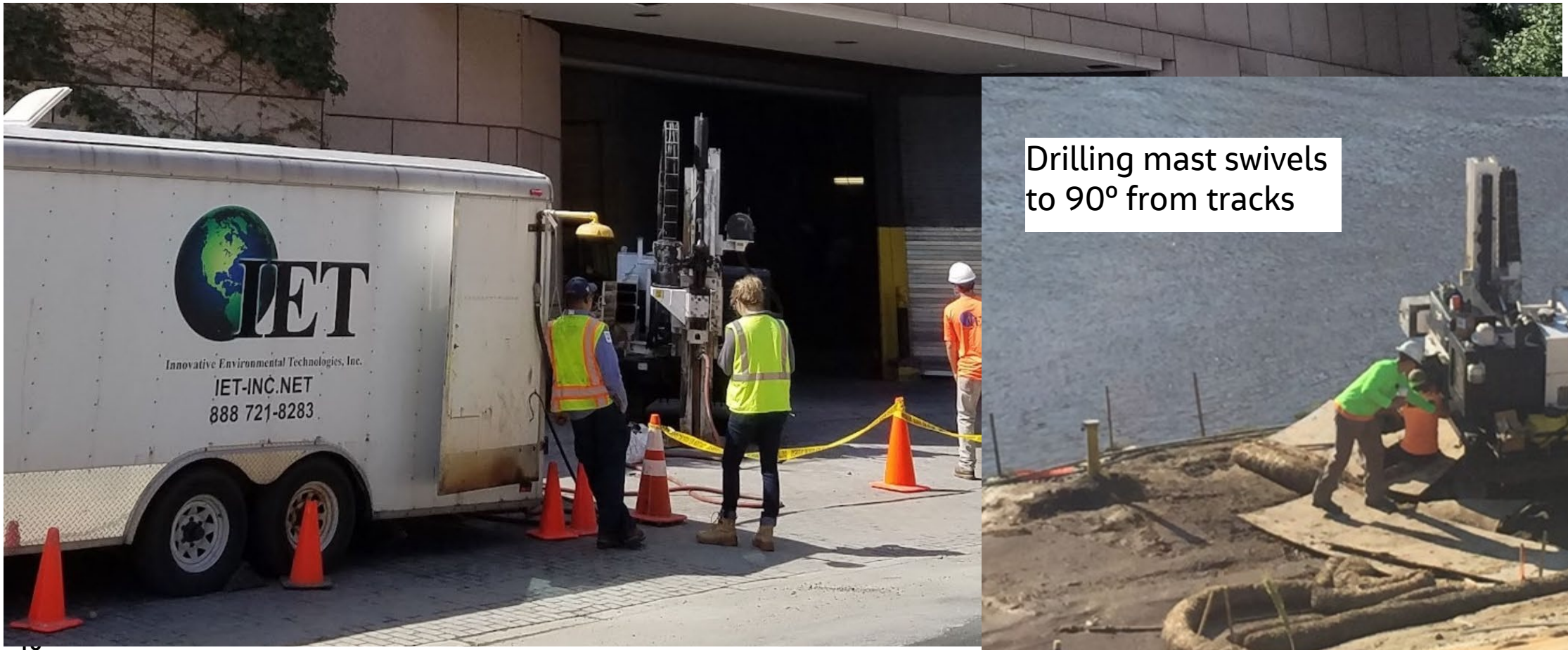
0′ 200′

Experimental Observations using Bunker Oil 4 Surrogate (roofing tar)



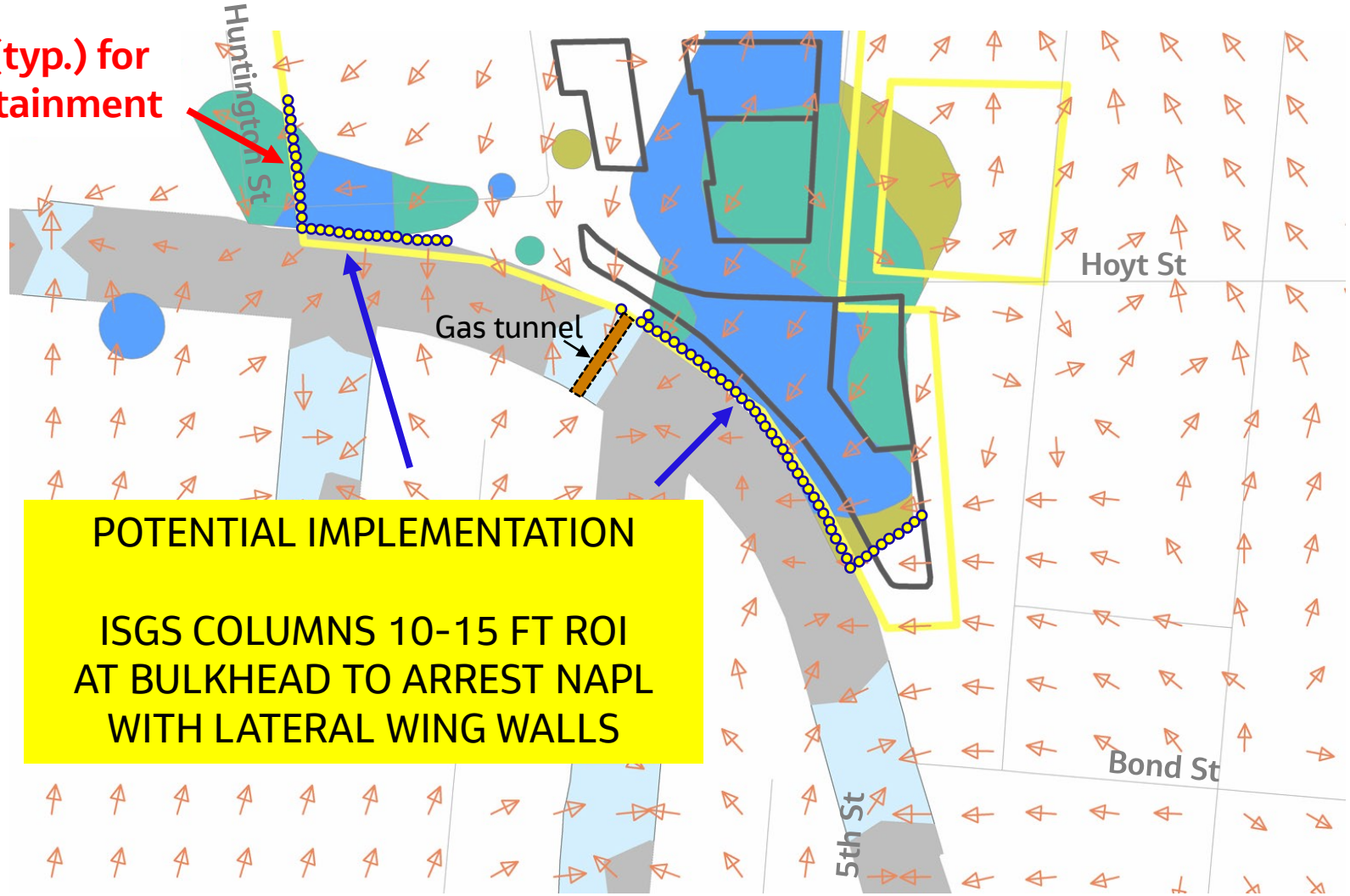
ISGS Technology is compact technology

- Used in tight spaces, low vertical clearance geo-probe platforms
- Several support trailers for reagent blending, etc.
- Low ground pressure equipment, can get close to bulkheads



Location of ISGS based on Groundwater Flow Directions

Wing wall (typ.) for lateral containment



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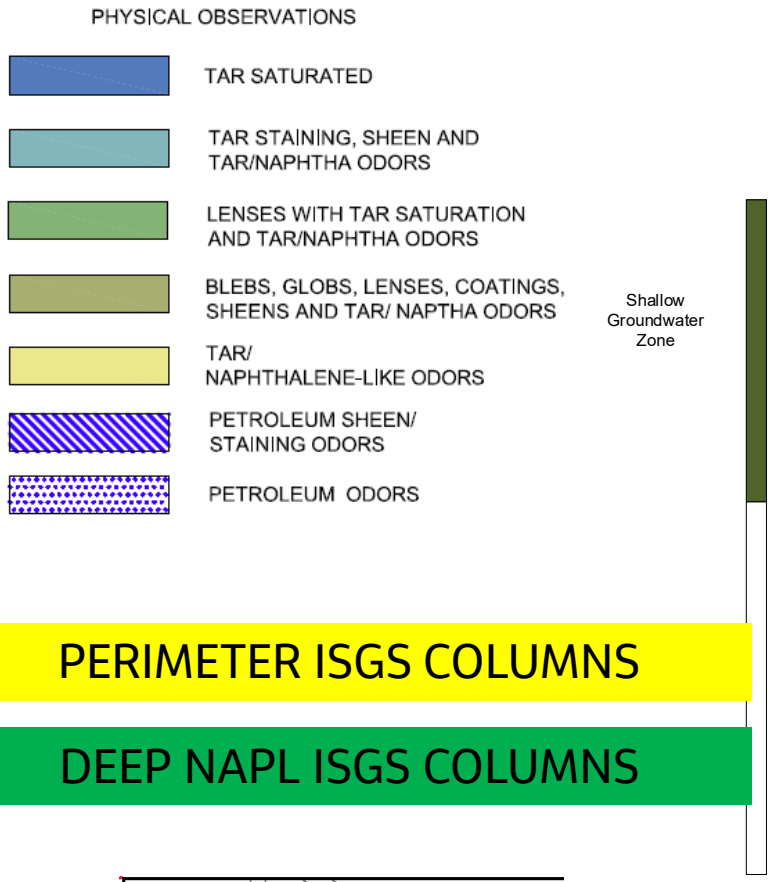
NAPL DISTRIBUTION 2005

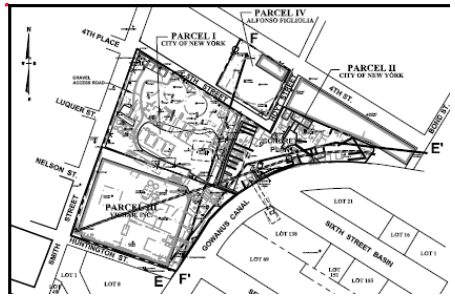
Immobilizes NAPL close to sheet pile Wall to prevent full depth flow into canal

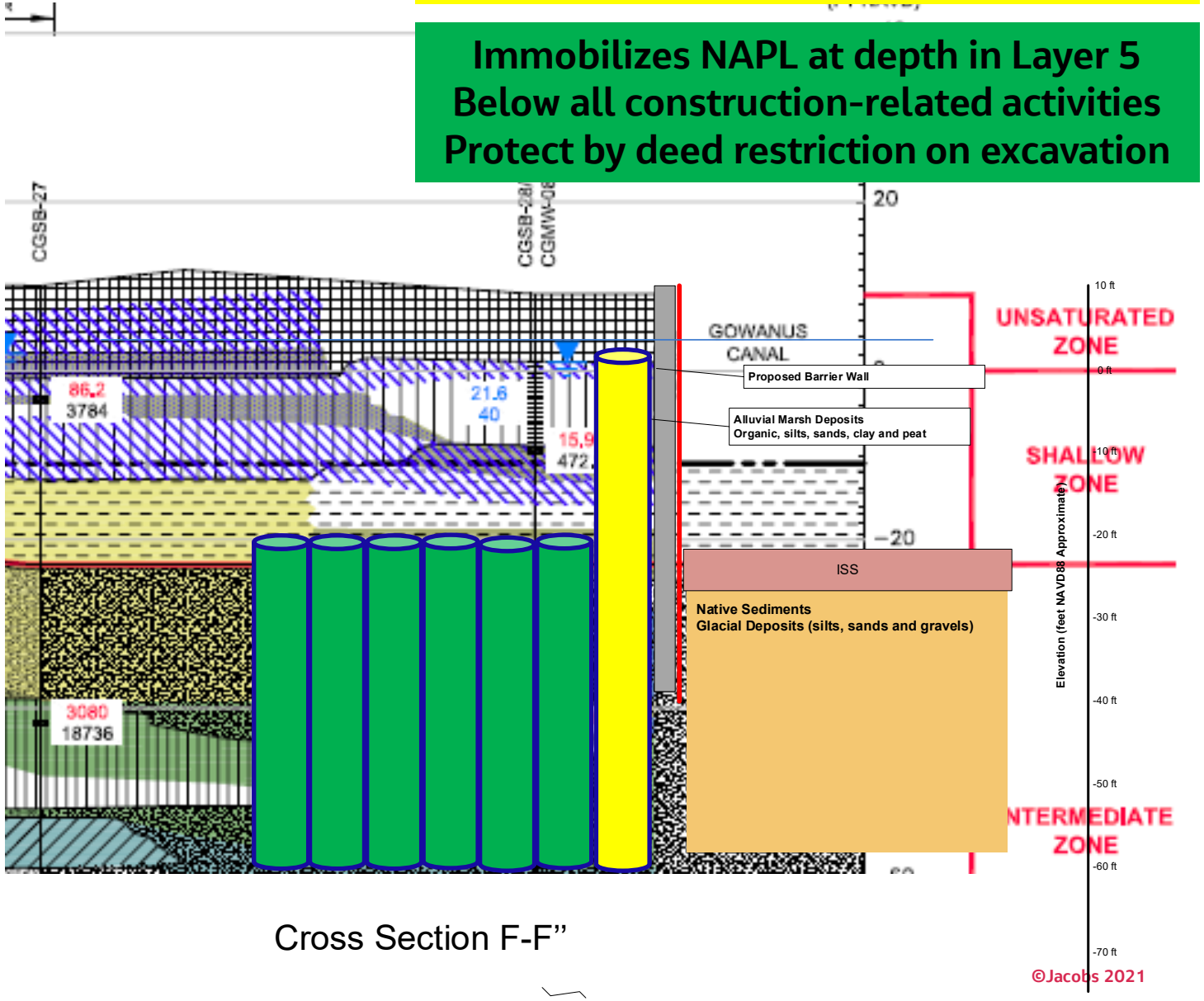
Immobilizes NAPL at depth in Layer 5 Below all construction-related activities Protect by deed restriction on excavation



PERIMETER ISGS COLUMNS

DEEP NAPL ISGS COLUMNS



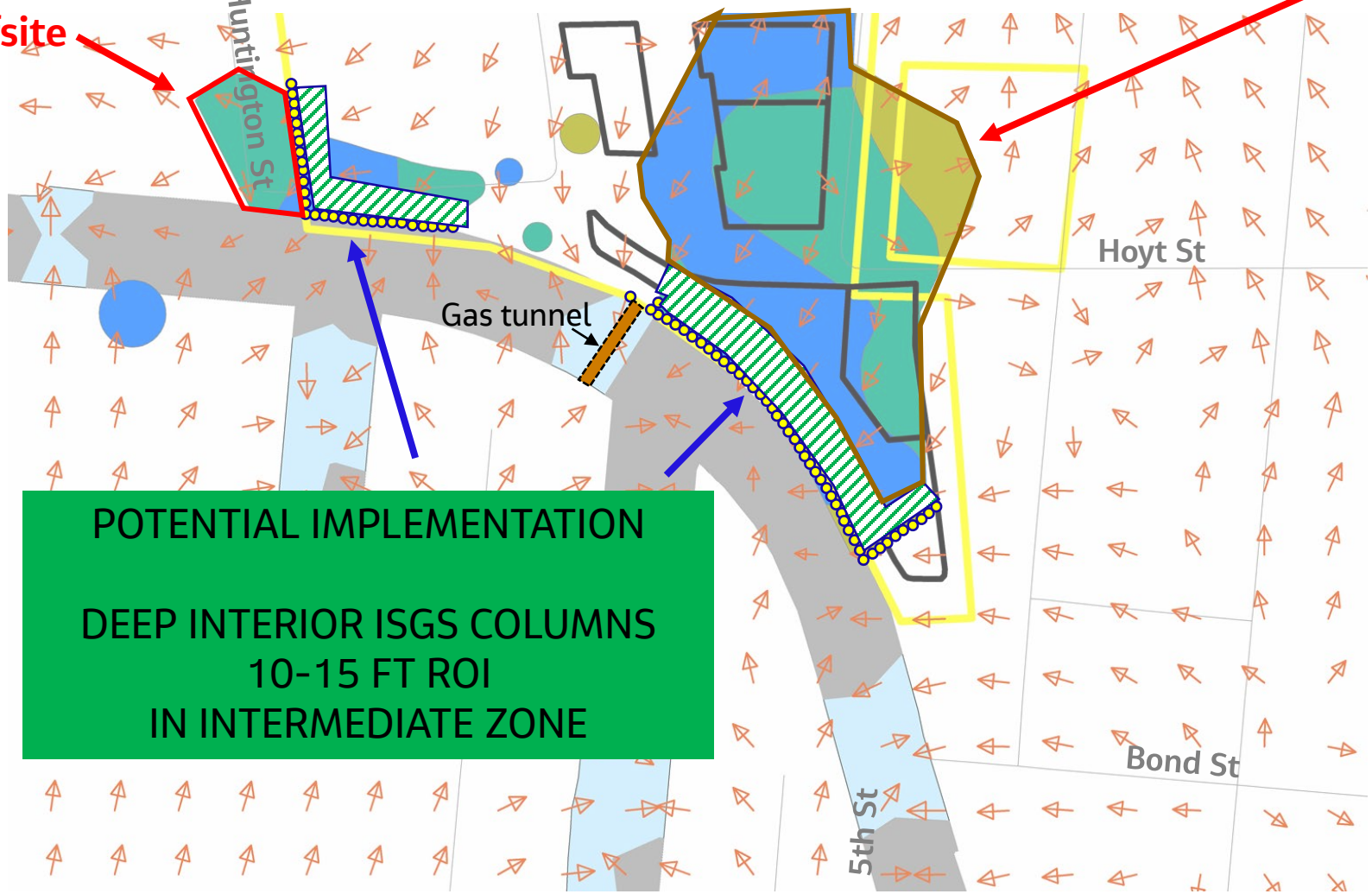


Cross Section F-F”

Location of ISGS Full-depth Perimeter & Wing Columns

This area already offsite

Upland area treated by another method?



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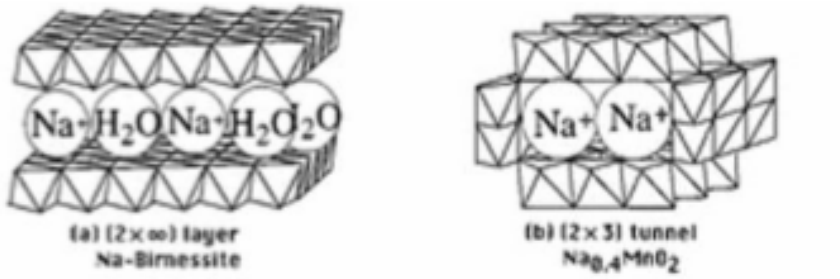
BACKGROUND SLIDES

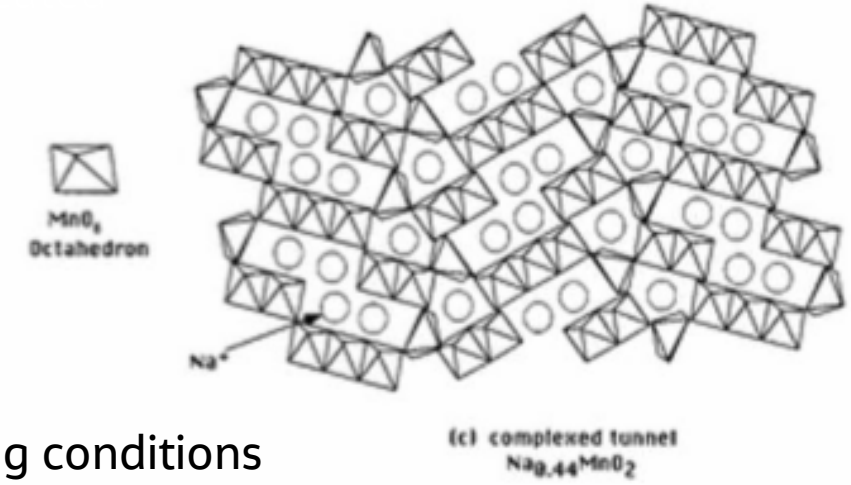
NEW MINERALS Formed

Key mineral formed is birnessite or $(Na,Ca,K)(Mg,Mn)Mn_6O_{14}.5H_2O$

Oxide precipitate



Layered-tunnel like structure



Mineral is stable under reducing conditions

Good recent technology overview available at:

http://carusllc.com/remediation/webinars/remediation-webinar-recordings/isgs-a-modernized-dnapl-stabilization-technology-update

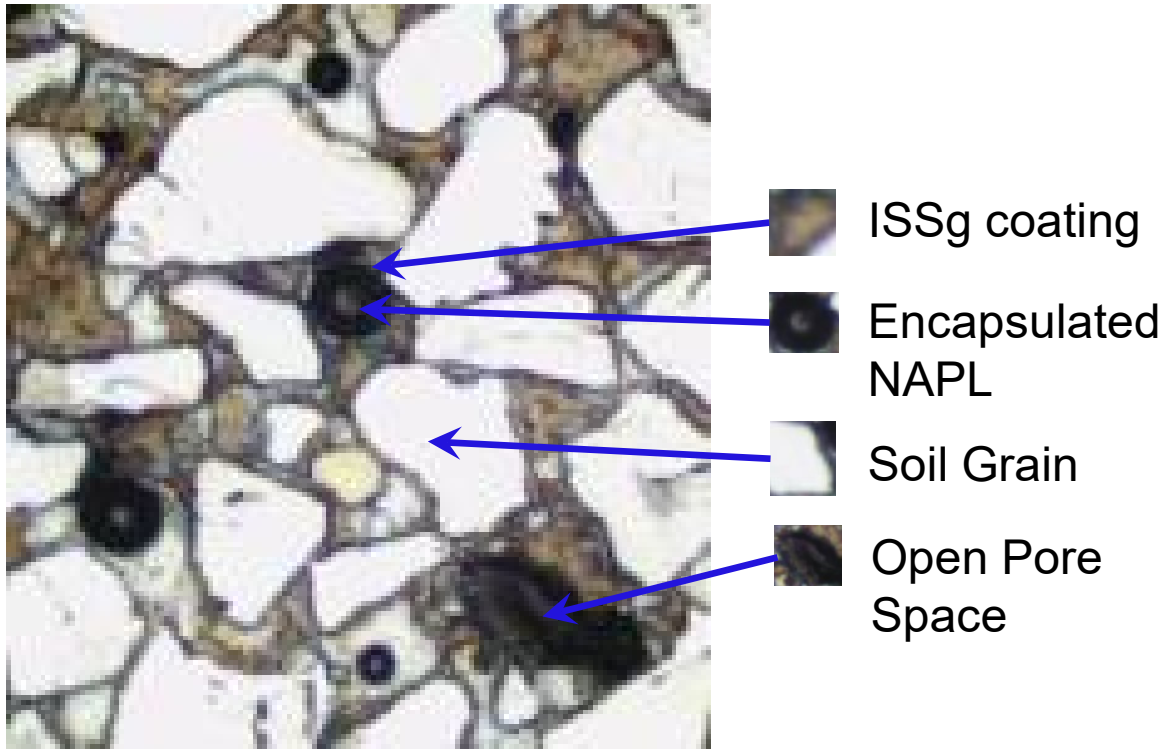
Field Sample (Day 5)

Stabilization through mineral Creation

- Provect-GS solution is injected into NAPL impacted media
  - Thin sections from site samples show MnO2 precipitates (e.g., Birnessite) at the NAPL-water interface, physically forming a crust/skin that immobilizes/encapsulates NAPL, coats soil grains and clogs pore space with other minerals (e.g., iron, silica, etc.)

Birnessite mineral

Birnessite precipitate/coatings on sand



Birnessite precipitates throughout NAPL impacted soil (microscope view)

In SITU GeOCHEMICAL Stabilization (ISGS)

- In ISS family of technologies, near geochemical end of spectrum
- Proprietary Na/K Permanganate, iron, silica and Organoclay (OC) blend (Provect-GS™)
- Reactions rapidly occur at NAPL-water interface reducing potential mobility
  - Creates insoluble MnO_2 precipitates (also Fe and Si) at the NAPL surface
  - NAPL surface coated, interior reactions increase NAPL viscosity

- Technology emerged in early 2000s. Approach evolved.

- Current formulation (Provect-GS) exclusively licensed by IET (from FMC) marketed via Provectus (IET subsidiary)

- Pilot- and full- scale applications on creosote and MGP; including project located in Fanwood, NJ

- Approved technology by USEPA Regions 4 and 8

Photographs courtesy of IET, Inc.

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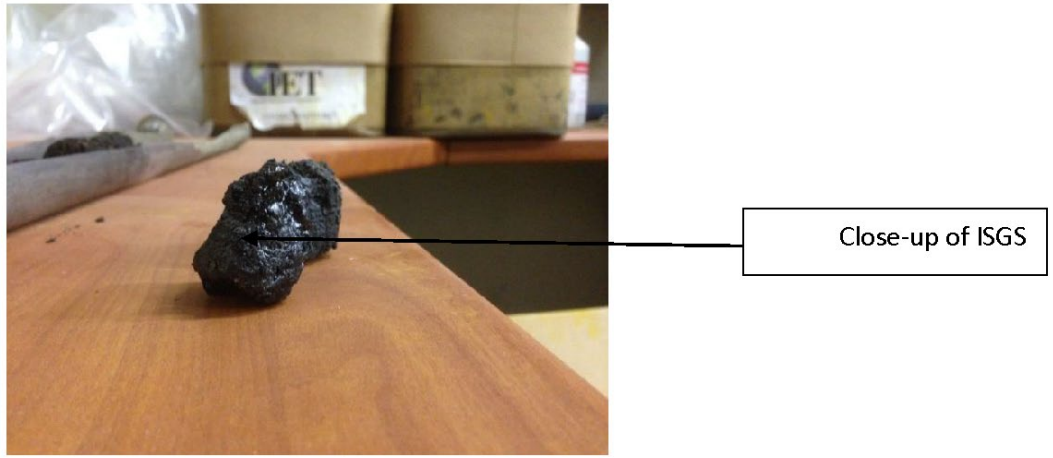
IET Innovative Environmental Technologies, Inc.

Example: ISGS at Fanwood, NJ Site

- Site impacted with coal tar NAPL from neighboring property
- 3-5 ft of NAPL in wells across site
- Soils and groundwater treated between depths of 5 to 10 ft
- 9,000 ft^2 treated. 80 injections at 44 locations at 2 intervals
- 5 to 10 psi injection pressure; ROI ~ 7.5 ft

- Single injection event in mid-2013. First follow up 10/13
- NAPL recovery dropped to zero in all 10 monitoring wells by 30 days and remained so for 2-year monitoring period
- Significant reductions in dissolved COCs
- Site closed and re-developed
- "Rock-like" NAPL pieces recovered from several core locations



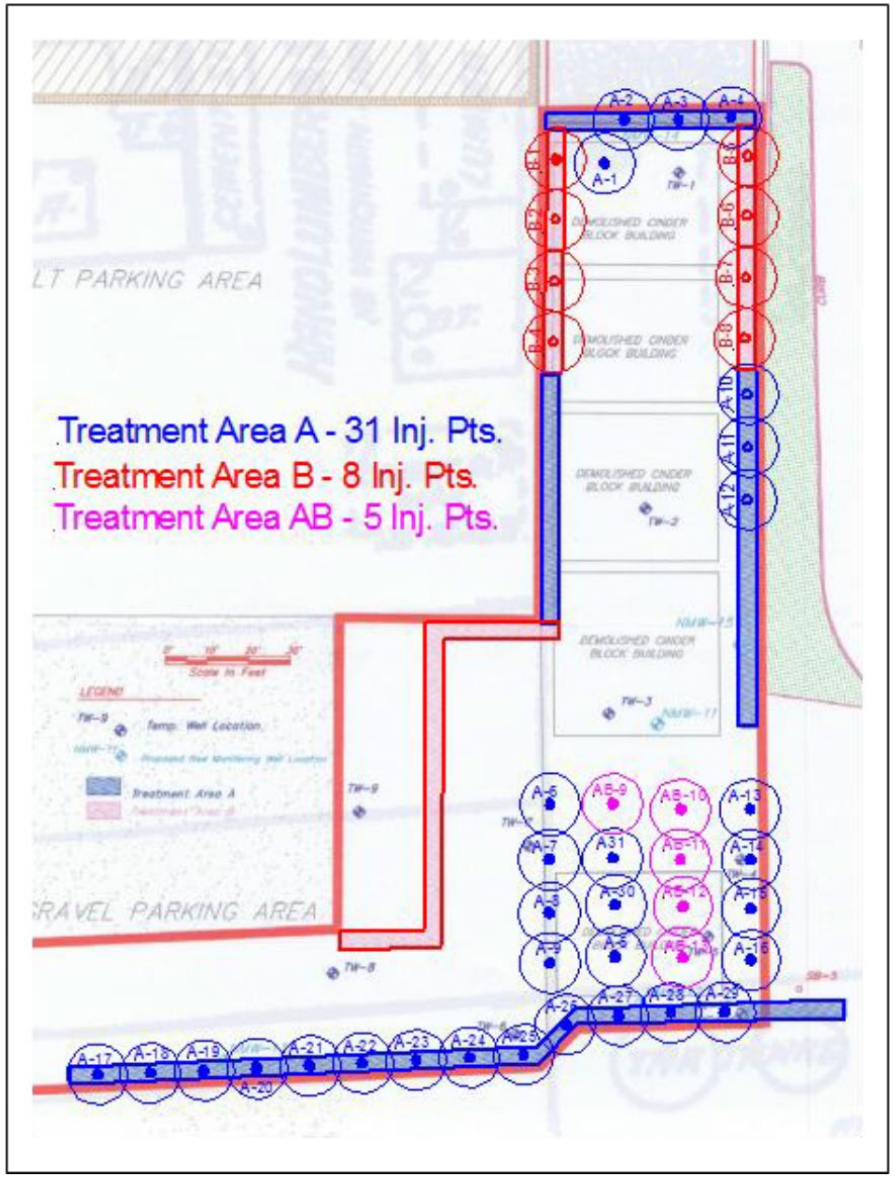


Figure 1. Site map showing the location of 44 in-situ injection points.